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Dissolved iron at subnanomolar levels in the Southern Ocean as determined by ship-board analysis

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Abstract

The biogeochemistry of iron was investigated in remote waters of the Antarctic ocean in the austral summer of 1995/1996. A sensitive flow injection analyser, based on in-line preconcentration and luminol chemiluminescence detection (FIA-CL), was used for underway surface measurements and vertical profiling during a fine scale survey in the Polar Front (PF) in the Atlantic sector of the Southern Ocean. Results indicated a dynamic environment with dissolved iron concentrations ranging from 0.05 to 0.3 nM. Distributions are consistent with chlorophyll *a* and fCO_2 suggesting a coupling with these parameters. The highest iron concentrations (0.3 nM) were found where chlorophyll *a* abundance was highest and CO_2 undersaturation the most pronounced. The vertical distribution (upper 500 m) revealed a nutrient type distribution with low subsurface values (0.1 nM) gradually increasing to ~0.3 nM at depth.

Keywords: Flow injection analysis; Iron; Seawater; Antarctica; Polar front

1. Introduction

The contrasting situation of low primary production in remote ocean waters in spite of replete nutrients (nitrate, phosphate and silicate), was first observed in the Antarctic ocean in the late twenties [1] and is known as the 'Antarctic Paradox'. Ever since the idea of deficiency of iron as essential trace nutrient in such a High Nutrient Low Chlorophyll (HNLC) area was introduced [2], many investigators have taken up the challenge to study the iron limitation hypothesis [3]. In the beginning these attempts were quite unfruitful due to the lack of sensitive analytical methods, and more notably, problems of contamination during sampling and sample processing [4].

Iron is obviously the most abundant element on board of a steel research vessel, so precautions need to be taken to prevent sample contamination as iron exists in ocean waters at very low levels. Concentrations ranging between 0.05 nM near the surface to around 2 nM in deeper waters [5–8] can be found. Higher values can be expected near the seafloor by diagenetic input [9,10], in coastal waters [8,10], upwelling areas [11], frontal systems [10] and areas affected by aeolian input [12].

The last two decades have shown major advances in the field of ultraclean working methods and ultratrace

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analysis. Until recently, the most widely applied technique to determine trace metals in seawater involved preconcentration and sea-salt separation by complexation with dithiocarbamates, extraction into an organic solvent, back extraction or digestion in acid solution followed by GF-AAS detection [13–15]. This method is very laborious, uses large amounts of sample and reagents and is not without risk of contamination due to the many pretreatment steps. Also, GF-AAS cannot be done on board because the instrument is large and sensitive to vibrations.

Recent developments involve flow injection analysis (FIA) [11,16–18] and voltammetric techniques like cathodic stripping voltammetry (CSV) [19–21] for ship-board measurements. Data can be obtained in virtual real-time, facilitating quick response to phenomena in the field. Also contamination control is improved because sources of contamination can be identified immediately and remedied.

We present here an automated FIA-CL device which is a modification of the method by Obata et al. [18,22] for measuring concentrations of total dissolved iron. The detection is based on the chemiluminescence produced by the Fe-catalysed oxidation of luminol by hydrogen peroxide [23]. The device was used for high resolution sampling to study frontal dynamics and biology in the Southern Ocean.

2. Experimental

2.1. Sampling

Samples were collected during cruise ANT XIII/2 (December 1995–January 1996) on board the German research vessel Polarstern in an area of about 130×123 km in the Polar Front (PF) at around 50°S, 10°E (Fig. 1). Surface samples were taken every hour during a Fine Scale Survey (FSS) from 2.1.96 (10:00 UT) until 5.1.96 (05:00 UT) while steaming in westerly direction along longitudinal transects 13 km apart. Just before and after the FSS, seven stations were occupied in the same area for vertical profiling of the upper 500 m of the water column.

Temperature, nutrients and chlorophyll *a* data of the surface were derived from Polarstern's pumping system located at the bow of the ship at 8 m depth. Silicate and nitrate were measured on a Technicon

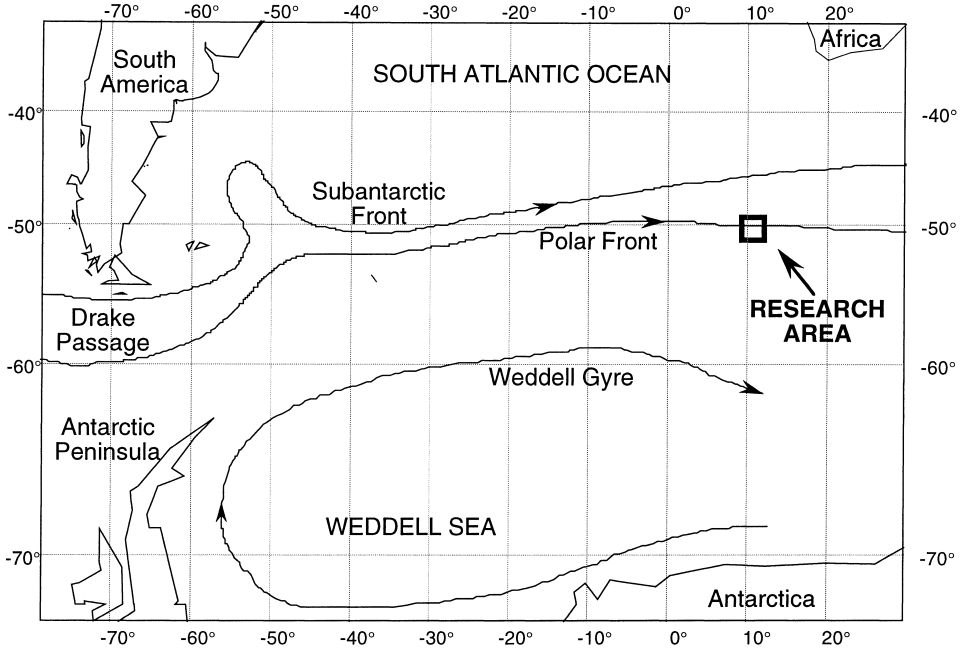

Fig. 1. The Atlantic sector of the Southern Ocean.

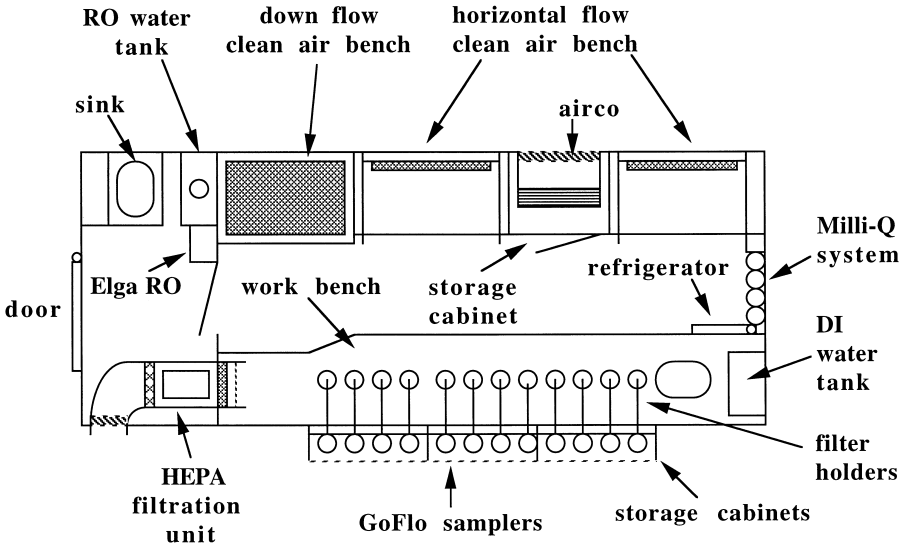

Fig. 2. Exposed view of the class 100 clean air container van.

Autoanalyser II system using established methods. Chlorophyll *a* was measured every 10 s with a Turner TD 10 flow-through fluorometer. Average values of 5 min intervals are presented. Using a Li-Cor infrared analyser fCO_2 was measured in the headspace gas of an equilibrator that was continuously supplied with surface seawater.

Analytical trace work was carried out in an overpressurised class 100 clean air van (Fig. 2), inside of which the analysts wore special antistatic lab coats and caps (Angelica, St. Louis, MO, USA), clogs (Schürr, Germany) and plastic gloves. The van is equipped with an Elgastat reverse osmosis filter and Millipore Milli-Q^{TM} water purification equipment delivering >18 MΩ cm deionised water (DI). It was modified into a recycling mode to produce double deionized water (DDI) with significantly lower iron concentrations than normal DI water (0.15 versus 0.6 nM, verified with FIA-CL).

2.1.1. Sampling of surface seawater

Surface sampling was done by pumping seawater into the clean air container van through a tube attached to a towing fish. Contamination from the ship was avoided by towing the fish at ∼5 m distance alongside the ship with the crane arm of a hydrographic winch, keeping it outside the wake. The fish was a homemade, 1 m long solid stainless steel, epoxy-coated torpedo of 50 kg with three fins at the tail. The fish remained stable at a depth of 0.5–1 m at speeds to a maximum of 10 knots. The sample tubing consisted of ∼15 m flexible reinforced PVC, 10 mm i.d. It was attached with tape and tie-raps to the fish and the stainless steel hydrowire. The tubing had been extensively cleaned with 1 M HCl and rinsed with DI water. The water was pumped on board with a Cole-Parmer Masterflex I/P variable speed modular pump drive model 7591-00 with an Easy-Load model 7529-00 pump head with silicone pump tubing. The seawater was filtered in-line at a flow rate of ∼0.5 l min^{-1} through a teflon filter holder containing a 143 mm diameter, acid-cleaned polycarbonate membrane filter with a pore size of 0.4 μm. Discrete samples were taken in 250 ml clean polyethylene bottles and acidified to pH 1.8 with triple quartz distilled (3QD) concentrated nitric acid (1 ml l^{-1}). All sample bottles had been cleaned by leaching in hot (60°C) 6 M HCl for at least 24 h followed by ample rinsing with DI water. Polycarbonate filters were soaked in 1 M hydrochloric acid for 1 week after which they were stored in DI water.

2.1.2. Sampling of deeper water

For vertical sampling of seawater, modified teflon coated PVC General Oceanics (Miami, FL, USA) GoFlo bottles of 11 l have been used. The drain cock

was replaced by a teflon stop cock. The black rubber spring was replaced by a titanium spring as rubber has a potential for contamination and loses its strength at increasing age and at low temperatures.

The samplers were cleaned by filling them in the home clean air laboratory with acidified DI water (pH∼2), using reagent grade HCl (J.T. Baker) and rinsed with DI water after at least 24 h. On board all the samplers were filled with seawater that was subsequently acidified to pH∼2 with reagent grade HCl and were left to stand for at least 24 h. Prior to further use they were emptied and rinsed with DDI water.

A winch with 1000 m 10 mm diameter Kevlar hydrowire was used with ten samplers attached at standard target depths of 25, 50, 75, 100, 150, 200, 250, 300, 400 and 500 m. A 35 kg lead filled PVC counterweight was used to keep the wire vertical. The samplers were tripped by teflon messengers with a stainless steel core.

After recovery, the samplers were mounted in storage cabinets outside the clean air container van and connected to the interior using teflon tubing going through the wall. The samplers were also connected with silicone tubing to the gasline system of the van for prefiltered pure nitrogen. The seawater was pressure-filtered in-line at 0.5 bar through acid-cleaned teflon filter holders containing 47 mm diameter, acid-cleaned polycarbonate membrane filters with a pore size of 0.4 μm. Ample water (500 ml) was used to rinse the tubing and filters. First some seawater was collected for nutrient analysis after which acid-cleaned 250 ml polyethylene sample bottles were rinsed and filled. The samples were acidified to pH 1.8 with 3QD concentrated HNO_3 (1 ml l^{-1}).

2.2. Apparatus

The device of Obata et al. [18] contained a column with the chelating resin MAF-8HQ and was designed to measure Fe(III) in unfiltered seawater samples that were weakly acidified (pH 3.2) before in-line filtration. It therefore measured a mixture of truly dissolved iron and pH 3.2 leachable iron. Our instrument measures total dissolved iron in strongly acidified filtered samples using preconcentration with TSK-8HQ. Using 0.4 μm filters we separate dissolved Fe species (dissolved Fe, colloidal Fe, (in)organically complexed Fe) from suspended particulate matter. Acidifying the filtrate to pH 1.8 releases all but the most refractory iron species into the dissolved form. It should be noted that before acidifying, the samples were left in the dark for 1 h to re-oxidise any present Fe(II) in the absence of photoreduction [24].

The analyser constructed by Obata et al. [22] is rather large, relying on four peristaltic pumps and 10 solenoid valves. Our analyser is a smaller, cheap benchtop instrument with the number of moving parts kept to a minimum. The miniaturised photon counting head has a built-in, high-voltage power supply and amplifier. It does not need to be cooled to decrease incident background radiation.

2.2.1. System description

The instrument (Fig. 3) is an assembly of commercially available components. An eight channel peristaltic pump (Gilson Minipuls 3) is transporting acidified sample, buffer, reagents and rinsing DDI water. The pump runs at 8 rpm to reach the nominal flow rate (see Fig. 3). The reagents are kept at a constant temperature of 25°C in a perspex thermostatised bottle box. High density polyethylene reagent bottles (Nalgene), polypropylene reagent straws (Bran and Luebbe), polycarbonate connectors (Cole-Parmer) and PVC pump tubing were used, while all the other tubing was 0.8 mm i.d. teflon FEP. The system was cleaned by slowly pumping 0.5 M HCl for several hours, followed by rinsing with DDI water.

A 6 cm long, 3 mm i.d. preconcentration column containing immobilised 8-hydroxyquinoline on hydrophilic vinyl polymer (TSK-8HQ) was prepared according to the method of Landing et al. [25] using Toyopearl HW-40C resin (TosoHaas, Germany). The column was installed in the sample loop of a Valco (VICI, Switzerland) six-port teflon rotary valve on an electrical actuator.

During a loading time of 4 min 15.6 ml sample at pH 3.5–4 passes over the column. A Valco four-port selection valve then switches and the column is rinsed with DDI water for 1 min to remove sea-salts. If the column would not be rinsed, the sea-salts still present in the dead volume of the column may precipitate after introduction in the system at the reaction pH of 9.5 and clog the detector. The iron is eluted with 0.3 M HCl in reverse flow direction. The eluent mixes and reacts with 0.1 mM luminol/0.3 mM TETA, 0.8 M ammonia and 0.1 M hydrogen peroxide before introduction in

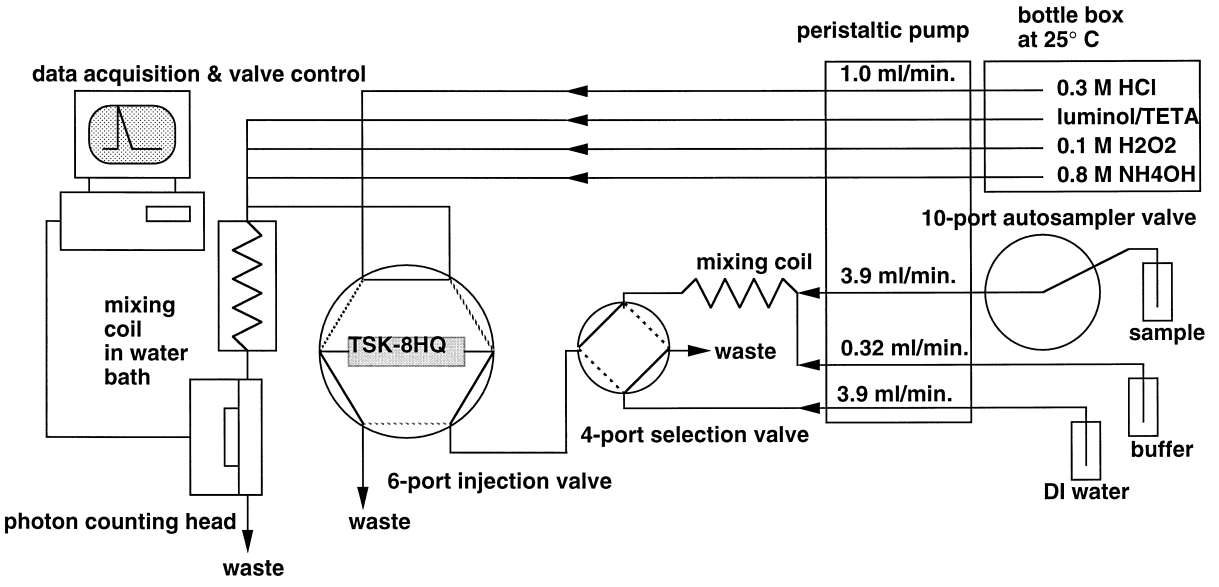

Fig. 3. Schematic diagram of the FIA-CL system.

the detector (Hamamatsu H6240-01, range 185–850 nm).

One analytical cycle of loading, rinsing and injection takes about 9 min. Autosampler valve (10-port), selector valve and injector valve were controlled via a home-made interface by software developed at the institute. The software was made in Visual BASIC™ running under Windows 95™.

The instrument was calibrated by the method of standard additions using peak area measurement. Additions were in the range 0.25–0.50–1.0–2.0 nM Fe using acicified low iron seawater collected at the sampling stations.

2.2.2. Reagent preparation

Concentrated acetic acid (HAc, 17 M) and concentrated nitric acid (14 M) were purified by means of triple sub-boiling distillation in a quartz still, that was placed in a clean air cabinet in the clean air room of the home laboratory. These 3QD products were collected in acid-cleaned teflon bottles and stored in plastic bags.

Clean concentrated ammonium acetate buffer (5 M, pH∼5), with a residual reagent contamination of ∼3 nM Fe, was made by mixing 300 ml of 3QD HAc with 300 ml ultraclean ammonia and diluting to 1 l with DDI water. Ammonia was made by purging for several hours at a gentle rate pure ammonia gas through DDI water in an all-teflon ice-cooled device. Dilute ammonium aceate buffer (0.2 M) was made by 25-fold dilution using DDI water.

0.3 M hydrochloric acid was made from concentrated HCl (Merck, suprapur, 10 M), 0.8 M ammonia by diluting 25% NH_4OH (Merck, suprapur) and 0.1 M hydrogen peroxide from 30% H_2O_2 (Baker Analyzed, J.T. Baker). TETA (triethylene tetramine, Merck) and luminol (3-aminophtalhydrazide, Sigma) were used as received. Luminol was dissolved with about 0.1 g NaOH (Sigma).

3. Results and discussion

3.1. System performance

3.1.1. Optimisation

Most of the optimised CL conditions of Obata et al. [22] were applied, except that we used lower H_2O_2 (0.1 M) and luminol (0.1 mM) concentrations. This prevented the formation of bubbles in the system and gave a significantly lower baseline and an improved signal to noise ratio.

Table 1
Ion exchange properties of TSK-8HQ for different metals and in different media

ELEMENT 500 ppm	TEC (μmol g^{-1}) DI water	DEC (μmol g^{-1}) DI water	DEC (μmol g^{-1}) Seawater	BTC (μmol g^{-1}) DI water	BTC (μmol g^{-1}) Seawater
Ni	152.2	145	128	128.5	82.9
Mn		115.8	61.1	96.7	19.6
Co		107.9	53.4	83.1	18.2
Cu	145.2	91.4	85	62.5	32.9
Fe(II)		78	–	42.3	–
Zn	159.6	70.7	60.9	45.4	31.6
Fe(III)		68.1	43.8	3.8	0.8
Mg			8.6		<0.7
Ca			6.4		6.6

TEC: Total Exchange Capacity, DEC: Dynamic Exchange Capacity, BTC: Breakthrough Capacity at 95% exchange efficiency.

3.1.2. Column properties

Column performance was investigated using the following three parameters as given by Landing et al. [25] (results summarised in Table 1):

1. Total exchange capacity (TEC, μmol metal/g of resin) was determined in batch experiments for Cu, Ni and Zn by shaking and equilibrating for 1 h a small, known amount of TSK-8HQ with 100 ml 50 ppm solution of metal at pH=5. After rinsing with DI water and elution with 10 ml of 1.0 M HCl/0.1 M HNO_3, the eluent was measured by FAAS (Perkin-Elmer 5100).
2. To study the behaviour of TSK-8HQ under flow conditions (3.9 ml min^{-1}) the dynamic exchange capacity (DEC) was determined for Cu, Ni, Zn, Co, Mn and Fe in DI water and seawater at pH 5. A 7 cm long 3 mm i.d. column containing 0.12 g TSK-8HQ was loaded with 100 ml 50 ppm of a metal, rinsed and eluted with 10 ml of 1.0 M HCl/ 0.1 M. The eluent was analysed by FAAS.
3. After breakthrough of a column metal can still be retained, although at a low efficiency. The breakthrough capacity at 95% binding efficiency (BTC) gives information on the amount of metal that can be retained quantitatively under flow conditions. To determine the BTC, the waste of the test solutions used above was collected in aliquots of 2.5 ml and measured with FAAS. The resulting breakthrough curves (not shown) were used to estimate the BTC.

The total exchange capacity was uniform for the metals investigated and was twice as low as the value of 294 μmol g^{-1} reported by Landing et al. [25]. Our value is more comparable with materials that use silica based carriers [26]. Probably the synthesis of our resin was carried out under less than optimal conditions. The smaller pore size of HW-40C carrier compared to HW-75F (50 Å versus >1000 Å), generally should offer a better surface per volume, thus having more binding sites. However, this may also cause lower access of the reagents to the inside of the carrier particles due to steric hindrance. Still, HW-40C was preferred for minimising back-pressure in the system because the particles are larger than HW-75F (50–100 μm versus 30–60 μm).

The dynamic exchange capacity was lower than the total exchange capacity for all metals. This can be expected as due to the short contact time of the test solutions with the column (~3 s), not all of the complexation sites were used. The dynamic exchange capacity in seawater was lower than in DI water, probably because of (in)organic complexation and the affinity of the TSK-8HQ for certain counterions in the test solution.

Breakthrough capacities at 95% exchange efficiency were considerably lower than the dynamic exchange capacity, because of the apparently slow kinetics of the ion exchange. Already after passage of a relatively small volume of test solution the efficiency drops below 95% although metals are still bound beyond this point. The same factors mentioned in the above paragraph apply for explaining the differences between DI water and seawater. The mutual differences between the metals are probably caused by a combination of factors, such as degree of (in)organic

complexation of the metal in the medium or different stability constants for each metal to the ligand immobilised onto the resin.

A special situation occurs for Fe(III), where the breakthrough capacities at pH 5 in both DI water and seawater are particularly low. This may be due to the capability of Fe to hydrolyse [27] resulting in it existing as hydroxides in water. These Fe hydroxides will precipitate to form colloids at the high concentration used for the test solution. As a consequence, Fe(III) will have less accessability to the complexation sites than the other metals and ion exchange kinetics will be slower. For comparison we repeated the experiment for Fe(II) in DI water at pH 5. Fe(II) is present mainly as the free ion which would explain the higher exchange capacities then for Fe(III). Although Fe(II) is the thermodynamically unfavoured form of iron in oxygenated water the pH 5 will slow down the oxidation of Fe(II) and stabilise the test solution [27].

At the much lower iron concentrations encountered in seawater, the breakthrough capacity would conceivably be higher as the relative amount of colloids is smaller. Also, acidifying samples as we do in this method, would lead to dissolution of the colloidal iron and make it available for ion exchange.

3.1.3. Selectivity

The dynamic exchange capacity results for major bivalent cations in seawater like Ca and Mg (Table 1) clearly demonstrate the selectivity of the column material for transition metals in general. With passage of 100 ml of seawater test solution the column is confronted with a total load of 1022 μmol Ca and 5366 μmol Mg. From this bulk only $6.4\times0.12=0.77$ μmol Ca and $8.6\times0.12=1.03$ μmol Mg is retained on the column, meaning that respectively 99.92% and 99.98% are rejected.

The selectivity of the TSK-8HQ column for Fe(III) (Fig. 4) was checked by scanning the signal in a wide range of pH values using a batch of filtered Atlantic seawater with an iron concentration of 0.57 nM (FIA-CL). Consistent with findings of Obata et al. [18], two plateaux were detected, the first between pH 2.6 and 4.5 when Fe(III) is quantitatively extracted. The second between pH 6 and 7 indicates that Fe(III) and Fe(II) are both extracted. At pH 8 a remarkable signal increase was observed, which may be caused by the retention of other trace elements.

Therefore, a matrix interference study was performed by adding to three seawater test solutions at different pH, a cocktail of elevated concentrations of some of the metals (Co, Mn, Cu, Cr and Ni), known to

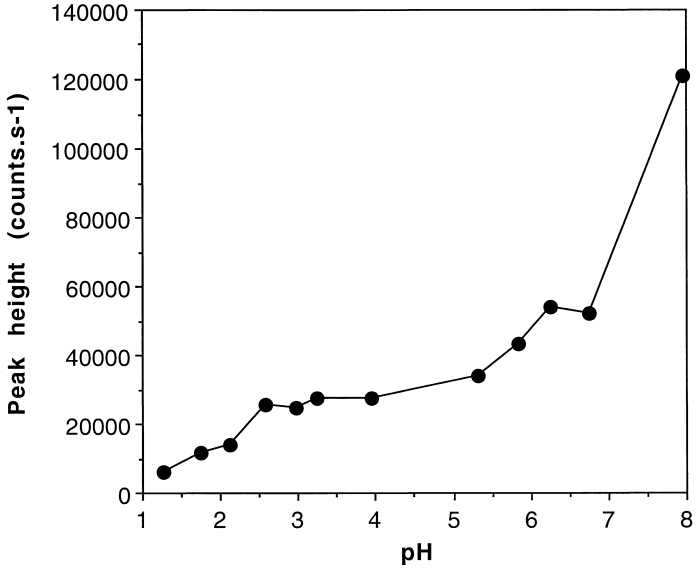

Fig. 4. System response as a function of sample pH.

Table 2
Signal recovery at different pH after addition to seawater (0.57 nM Fe) of a cocktail of 10 nM of Co, Mn, Cu, Cr and Ni

pH	Recovery %
3.15	106.9
6.25	93.9
7.95	134.7

be interfering with the CL reaction [18,28] (Table 2). At pH 3.2 and 6.3 no interference from these ions was detected, whereas at natural pH (∼8) a positive interference was observed. This would indicate that these ions are apparently retained by the column with such an efficiency, that when eluted, they co-react with Fe in the CL reaction.

3.1.4. Analytical performance

Typical blank and detection limit (three times standard deviation) values are averaging 0.022±0.007 nM (n=10) and 0.021 nM respectively. The blank is mostly caused by the DDI water that is used to rinse the TSK-8HQ column and is determined by measuring the peak that results from loading the column for 1 min with DDI water. Concentrated HNO_3 (3 nM residual Fe) and 5 M NH_4Ac (3 nM residual Fe) contributed respectively 3 and 9 pM to the blank and were deemed neglible. This was confirmed by comparing the signals from a normally treated sample and one spiked with extra acid and buffer.

Only one column was used continuously during the cruise and did not show signs of any deterioration in performance, as the sensitivity remained rather constant with an average of 29953±7932 (n=10) counts nM^{-1}. These calibration curves had an average correlation coefficient of 0.996±0.003.

Accuracy was checked by regular measurement of NASS-4 reference seawater (National Research Council of Canada). Results: 1.88±0.15 nM Fe (n=9), certified value=1.88±0.29 nM Fe. The precision was found to be within 2–5% in the whole working range of concentrations (0.05–2 nM). An intercomparison with the classic solvent extraction was made by re-analysing samples from a station of 1992 cruise ANT X/6. The profiles are shown in Fig. 5 and compare well for 3-year old samples. The differences could be caused by slow dissolution of some refractory iron species during the years of storage at pH 1.8.

3.2. Application

Not only that all possible precautions have to be taken to assure analytical reliability of a dataset, the

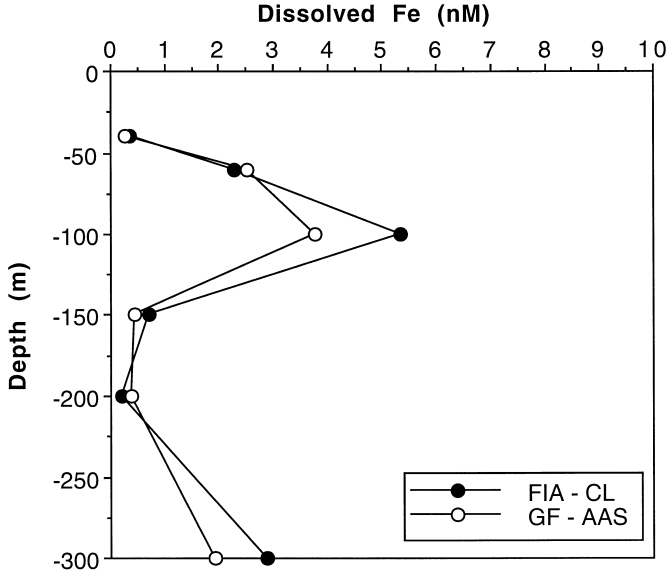

Fig. 5. Intercomparison between solvent extraction / GF-AAS (analysis 1993, open symbols) and FIA-CL (re-analysis 1995, closed symbols) for station 905 at 48°S, 6°W, sampled on 29.10.1992 during cruise ANT X/6.

results should also show oceanographic consistency [29]. This means that the observed distributions should relate to the relevant hydrographic, chemical or biological features of the research area. For the mere sake of comparison, some of these features will be shown here, although it should be noted that they will be discussed in more detail in the appropriate oceanographic journals.

The Southern Ocean is dominated by the Antarctic Circumpolar Current (ACC) flowing uniformly around the Antarctic continent towards the east, driven by strong westerly winds (Fig. 1). The ACC is separated from the other oceans by a meandering frontal system, comprising the Subantarctic Front (SAF) and the Polar Front (PF). The region between the SAF and the PF is the Polar Frontal Zone (PFZ). The PF features a fast flowing jet ($\sim$20 cm s^{-1}) relative to the slower moving ($\sim$5 cm s^{-1}) watermasses of the ACC [30]. South of the PF the ACC is characterised by cold waters with high nutrient concentrations, whereas north warmer waters are found with depleted nutrient concentrations, most notably for silicate (Fig. 6(a) and (b)). The PF is on the level of resolution of the FSS more like a transition region and is defined here, rather arbitrarily, as the 4.5°C isotherm. The isotherms are dense here and their position agrees well with a steep gradient of silicate around the 7 μM isoline.

The Polar Frontal region of the South Atlantic Ocean has been described as an area favourable for diatom blooms due to the presence of sufficient light and major nutrients, as well as the supply of iron from continental sources [10]. It has been speculated that, while flowing through and beyond the Drake Passage, the PF picks up iron from the shallow waters above the continental shelf areas of South America and the South Sandwich Islands [31]. Typical examples of this continental shelf input are: the nearshore Gerlache Strait (300 m depth) near the tip of the Antarctic Peninsula, where high dissolved iron concentrations of around 7 nM were found [7], and the shelf of Signy Island (South Orkneys, 200 m depth), further east off the tip of the Peninsula, where the dissolved iron concentration amounted to even 60 nM [9]. No data are available from the waters over the Patagonian shelf, where a similar situation should exist.

While flowing eastward iron would be removed from the water column by sinking biogenic particles, so iron should therefore decrease its concentration in easterly direction. It would decrease even stronger during spring blooms, as for instance observed in the PF during cruise ANT X/6 in the early austral spring of 1992 at 50°S, 6°W. Then, a bloom developed at an average iron concentration in the upper 150 m of 1.8 nM (chl. *a*: at 0.7 μg l^{-1}), which decreased to 1.1 nM (chl. *a*: at 1.3 μg l^{-1}) in 3 weeks time between two longitudinal transects [10]. The iron concentration may very well have further decreased with time and longitude to values comparable to those found in the present study, although it was carried out in a different year.

The surface iron distribution in the area (Fig. 6(c)) showed some patchiness and concentrations were slightly enhanced (0.3 nM), compared with deeper waters (0.1 nM). This may have been the result of surface orientated phenomena, such as episodic aeolian deposition of continental dust derived from South America, or the melting of icebergs. Icebergs contain at least 20 nM Fe [31] and could contribute locally to the surrounding waters. Enhanced concentrations of 1–9 nM total dissolvable Fe in unfiltered samples have been observed in the wake of an iceberg [31]. The fact that during this expedition no icebergs were encountered in the PFZ (in contrast to ANT X/6) [32], could be an indication that icebergs are not present there throughout the year or even not every year. Remarkable short-term shifts in the iceberg distribution have been observed before in the same area [33].

The patchiness of the iron distribution was rather well reflected by the chlorophyll *a* variations (Fig. 6(d)), ΔfCO_2 (Fig. 6(e)) and the nutrients distribution. Chlorophyll *a* is mainly concentrated near the Polar Front in the northern part of the research area in west-east direction, but a broad zone is extending to the south, centered around the 10.2°E meridian. The same holds for ΔfCO_2 and to a lesser extend iron. Interestingly, coinciding with this chlorophyll *a* zone, there also seems to be a decrease of silicate (Fig. 6(b)) and nitrate (Fig. 6(f)) in the high nutrient area south of the PF.

The similarity between these datasets demonstrates that where iron is present, in apparently still non-limiting amounts, phytoplankton is blooming (here dominated by large diatoms who have a relatively high physiological demand for iron). As iron is involved in the photosystems of algae, and light

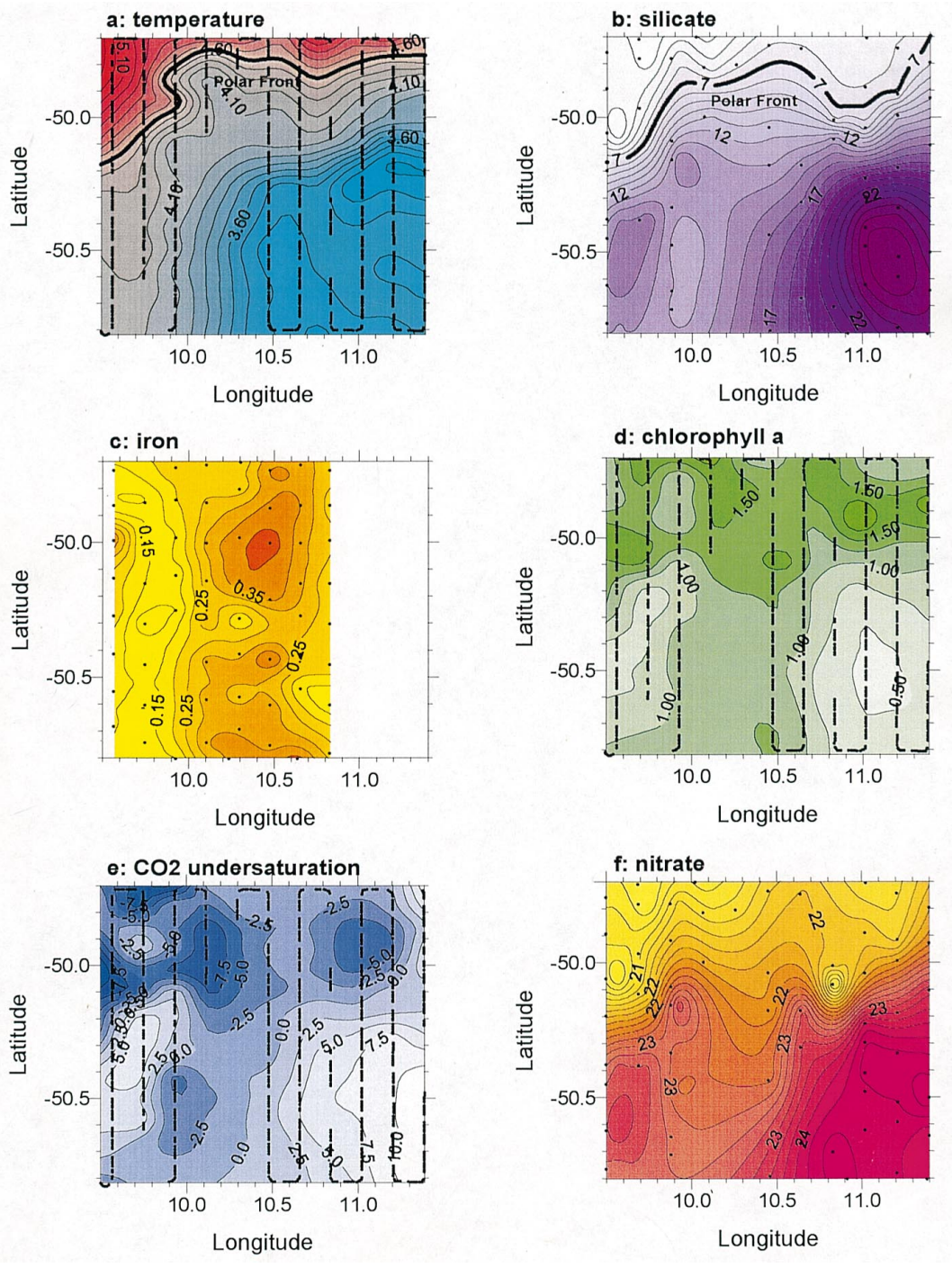

Fig. 6. Surface distributions in the research area. (a) temperature (°C). (b) silicate (μM). (c) dissolved Fe (nM). (d) chlorophyll *a* (μg l^{-1}). (e) ΔfCO_2 ($fCO_{2\ seawater}$–$fCO_{2\ atmosphere}$, μatm). (f) nitrate (μM).

conditions improve in the PF during spring, photosynthesis (chlorophyll *a*) will be enhanced. Iron is also needed as enzymatic co-factor in the nitrogen metabolism of algae [34]. Hence the observed decrease of nitrate in the presence of iron. Silicate decreases as diatoms use it for their cell walls. CO_2 is being taken up actively from the seawater by the phytoplankton, leading to undersaturation relative to the atmosphere.

The time delays between iron supply, diatom bloom conditions and CO_2 gas exchange cause offsets in their distributions. Moreover, there is a discrepancy in sampling depth of the several parameters and also a higher sampling frequency for chlorophyll *a* and fCO_2 determinations.

The seven vertical profiles did not show much variation and are presented as averaged concentrations (Fig. 7). They revealed relatively higher iron (~0.2 nM) in the upper 50 m, while below the euphotic zone at 100 m depth iron was very low (0.1 nM) but then increased to about 0.3 nM at 500 m. The vertical profiles compare well with previously reported profiles from the Drake Passage during austral autumn 1989 [7].

4. Conclusion

We developed a sensitive instrument to measure total dissolved iron in seawater with high accuracy. It has been successfully applied as a ship-board analyser to measure the lowest iron concentration that can be encountered in the oceans. High resolution underway sampling revealed considerable small scale variation in the surface distribution of iron, appearing to be consistent with similar variability of biological and chemical parameters. The vertical distribution was similar with previously reported data.

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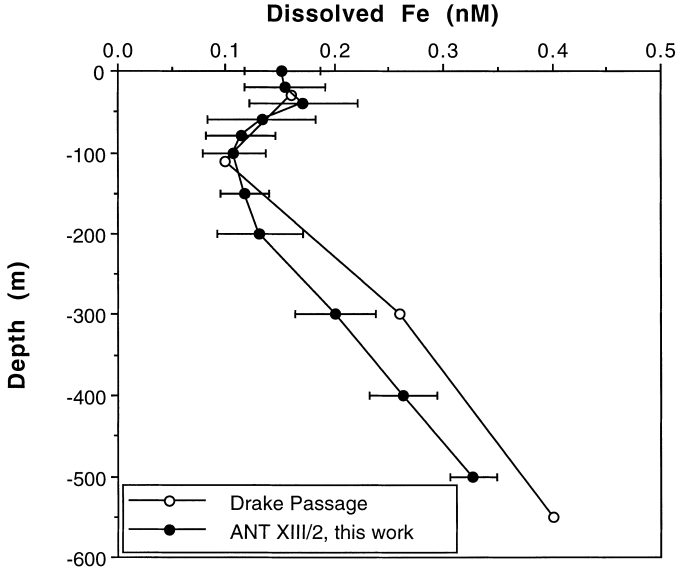

Fig. 7. Averaged total dissolved iron concentrations at seven stations in the upper 500 m in the FSS area as compared with Drake Passage station 2 from Martin et al. (1990). The error bars represent natural variability in the research area. The analytical error falls within the size of the used symbols.

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